

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
30 October 2003 (30.10.2003)

PCT

(10) International Publication Number  
WO 03/089551 A2(51) International Patent Classification<sup>7</sup>: C10M

(21) International Application Number: PCT/US03/11868

(22) International Filing Date: 15 April 2003 (15.04.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/373,161 16 April 2002 (16.04.2002) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

## Published:

— without international search report and to be republished upon receipt of that report

(48) Date of publication of this corrected version:

24 December 2003

(15) Information about Correction:

see PCT Gazette No. 52/2003 of 24 December 2003, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ENVIRONMENTALLY COMPATIBLE ADDITIVES FOR AQUEOUS LUBRICANTS

(57) Abstract: Lubricating compositions, containing non-modified and modified multifunctional, polyionic copolymers and an aqueous lubricating medium, and methods for making and using such compositions are described herein. The lubricating compositions are applied to metal oxide surfaces, which are in contact with each other. The copolymers can serve as a surface protective boundary layer for the sliding surfaces, or they can also be used for the immobilization of further molecules, which can modify the tribological properties of the surfaces.

WO 03/089551 A2

**ENVIRONMENTALLY COMPATIBLE ADDITIVES  
FOR AQUEOUS LUBRICANTS  
PRIORITY CLAIM**

This application claims priority to U.S.S.N. 60/373,161, entitled  
5 “Environmentally Compatible Additives For Aqueous Lubricants”, filed  
April 16, 2002.

**BACKGROUND OF THE INVENTION**

The present invention is generally in the field of tribology and  
specifically relates to applying lubricating compositions to surfaces to reduce  
10 the friction coefficient and wear on the surfaces.

When surfaces of a machine or device rub against each other, a  
friction force results, along with wear in the surfaces. The wear reduces the  
ability of the machine or device to function properly and efficiently. The  
frictional resistance can be reduced in a number of manners, such as by  
15 changing the structure of the surface, the material used, and/or by adding a  
lubricant between the surfaces. Lubricants separate the sliding surfaces by  
forming a film, and thereby reduce the frictional resistance and wear.  
However, under load increases and increased sliding speed, many lubricants  
break down. In the case of oil-based lubricants, the oil heats up with  
20 increases in speed and pressure, causing the lubricant to break down.  
Further, many oil-based lubricants are not suitable for industries, such as the  
food and beverage industry, which require the lubricant to not contaminate  
the food that is produced.

Water is an attractive alternative to conventional lubricating oils. It  
25 has ecological, health, safety, and economic advantages as a lubricant, as  
well as excellent heat-transfer properties. Therefore water serves as a  
coolant to the sliding surfaces. However, it has the disadvantage of a low-  
pressure coefficient of viscosity, which decreases its ability to support high  
loads. Nature solves this problem by coating the sliding surfaces *in vivo* with  
30 a “smart” material, cartilage, that changes in response to pressure and holds  
on the surface immobilized chains of biomolecules, which can function as  
boundary lubricants.

Most of the literature concerning lubrication by aqueous media is divided into articles dealing with (1) biological lubrication in the human body (Jay GD et al., J. Biomed. Mat. Res., 40(3): 414-418 (1998); Schwarz IM & Hills BA, Brit. J. Rheumatology, 37(1): 21-26 (1998); Smith AMA et al., Int. J. STD & AIDS, 9 (6):330-335 (1998); Widmer MR et al., Tribology Letters, 10(1-2): 111-16 (2001); Xiong DS & Ge SR, WEAR, 250: 242-45 (2001)), (2) lubrication of ceramics (Basu B et al., WEAR, 250: 631-41(2001); Chen M et al., Tribology Letters, 11(1): 23-28 (2001); Francisco A et al., Tribology Transactions, 45(1): 110-16 (2002); Saito T et al., WEAR, 247(2): 223-30 (2001); Umehara N & Kato K, J. Japan. Soc. Tribologists, 42(11): 879-85 (1997)), geological effects involving water (Regenauer-Lieb K et al., Science, 294(5542): 578-80 (2001)), (3) hydraulic pumps (Wang D et al., Indust. Lubric. and Tribology, 53(5): 211-16 (2001)), and (4) oil-in-water emulsions (Ratoi-Salagean M et al., Proceedings Inst. Mech. Engin. Part J: Journal Engin. Tribology, 211(J3): 195-208 (1997) and Ratoi-Salagean M et al., Tribology Transactions, 40(4): 569-78 (1997)), or rubber tires on roads (Veith AG, Rubber Chem. Technol., 69(5): 858-73 (1996)). However, relatively few articles address the use of a single-phase aqueous lubricant containing a boundary lubricating additive for the lubrication of metal contacts.

Plaza S et al., WEAR, 249 (12): 1077-89 (2001) describes a polyoxyethylene diphosphate derivative that appears to show some anti-wear and friction reduction activity in aqueous solution. At a load of 5N, all samples tested showed friction coefficients at 5N of around 0.1. Lei H et al., WEAR, 252(3-4): 345-50 (2002) describes a fullerene-styrene sulfonic acid copolymer, which shows low (0.3) friction coefficient at the lowest loads reported (100 N). The wear scar is shown to be very sulfur rich after the wear tests. Duan B & Lei H, WEAR, 249(5-6): 528-32 (2001) reports the use of colloidal polystyrene as an additive to aqueous fluids such as triethanolamine aqueous solution and a water-soluble zinc alkoxyposphate (OPZ) solution. The addition of colloidal polystyrene to an aqueous base

fluid appears to have a beneficial effect on the wear behavior of steel, as demonstrated by the maximum non-seizure load. However, the wear-scar diameter is not significantly reduced compared to the wear-scar diameter using a colloid-free solution, and no friction-reducing behavior is disclosed.

5 Hollinger S et al., Tribology Letters, 9(3-4): 143-151 (2000) reports the use of vesicular and lamellar systems, suspended in phosphate-containing solutions, which appear to reduce friction in interfaces between brass and tungsten.

10 Multifunctional copolymers described in U.S. Patent Nos. 5,462,990 and 5,627,233 and WO 98/47948 all to Hubbell *et al.* have been used in as surgical sealants and in analytical devices. U.S. Patent No. 5,462,990 and 5,627,233 to Hubbell *et al.* discloses multifunctional polymeric materials for use in inhibiting adhesion and immune recognition between cells and tissues. The materials include a tissue-binding component (polyionic) and a tissue

15 non-binding component. In particular, Hubbell discloses various PEG/PLL copolymers, with molecular weights greater than 300, with structures that include AB copolymers, ABA copolymers, and brush-type copolymers. These polymers are being commercially developed for use as tissue sealants and to prevent surgical adhesions. WO 98/47948 by Hubbell *et al.* describes

20 grafted polyionic copolymers that are able to attach to biological and non-biological samples in order to control cell-surface and cell-cell and tissue-surface interactions in biomedical applications. WO 00/065352 by Hubbell et al. describes polyionic coatings in analytical and sensor devices, which promote specific recognition of a target analyte and at the same time

25 minimize non-specific adsorption of other molecules in the sampling solution. However, these materials have never been used as lubricants.

There is a need for improved lubricating compositions. In particular there is a need for compositions which can reduce friction in metal oxide surfaces.

30 Therefore, it is an object of the invention to provide a stable polymeric material that can be added simply, quickly and cost-effectively to

an aqueous medium to produce an environmentally friendly, aqueous lubricant.

It is a further object of the invention to coat metal oxide surfaces and other charged surfaces with a lubricating composition to reduce the friction coefficient and wear on the surfaces.

### BRIEF SUMMARY OF THE INVENTION

Lubricating compositions, containing non-modified and modified multifunctional, polyionic copolymers and an aqueous lubricating media, and methods for making and using such compositions are described herein. The lubricating compositions are applied to metal oxide or other charged surfaces which are in contact with each other. The copolymers can serve as a surface protective boundary layer for the sliding surfaces, or they can also be used for the immobilization of further molecules, which can modify the tribological properties of the surfaces.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A depicts the chemical structure of a graft copolymer with a polycationic backbone, poly(L-lysine)-g-poly(ethylene glycol) (PEG-g-PLL), for surface modification of negatively charged surfaces.

Figure 1B depicts the chemical structure of a PEG-g-PLL polymer that is functionalized with biotin at the terminus of part of the PEG side chains.

Figure 1C depicts the chemical structure of a graft copolymer with a polyanionic backbone, poly(L-glutamic acid)-g-poly(ethylene glycol) (PEG-g-PLG), for surface modification of positively charged surfaces.

Figure 1D depicts the chemical structure of a PEG-g-PLG polymer that is functionalized with biotin at the terminus of part of the PEG side chains.

Figure 2 is a pictorial representation of multifunctional polymers adsorbed on to a surface. The top portion of Figure 2 contains the chemical structure of PLL-PEG and a pictorial representation of PLL-PEG adsorbing onto a negatively charged oxidic surface. The bottom portion of Figure 2 contains a pictorial representation of graft copolymers (a) and block

copolymers (b) formed from cationic components (heavy line) and poly(ethylene glycol) (light line). The dots at the ends of the light line represent specific molecules, which can be attached to the tips of the PEG chains.

5           Figure 3 is a graph of time (minutes) versus amount of PLL(375)-g[5.6]-PEG(5) ( $\text{ng}/\text{cm}^2$ ) adsorbed on three different metal oxide surfaces ( $\text{Nb}_2\text{O}_5$ ,  $\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_2$ , and  $\text{TiO}_2$ ).

          Figure 4 is a graph of isoelectric point versus amount of adsorbed polymer, PLL(375)-g[5.6]-PEG(5), ( $\text{ng}/\text{cm}^2$ ) for three different metal oxide  
10           surfaces ( $\text{Nb}_2\text{O}_5$ ,  $\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_2$ , and  $\text{TiO}_2$ ).

          Figure 5 is a pictorial representation of the pin-on-disk, sliding geometry used in testing the lubricant formulations. The dotted area designates the lubricant formulation. The dark, shaded rectangle designates the pin.

15           Figure 6 is a graph of friction force (N) versus load (N), used to determine friction coefficients for two different architectures of PLL-PEG, (1) PLL(20)-g(3.4)-PEG(2) and (2) PLL(20)-g[3.4]-PEG(5), as boundary lubricant additives for a steel-glass sliding couple.

          Figure 7 is a graph of load (N) versus friction force (N), used to  
20           determine friction coefficients for various sliding couples in the presence of PLL(20)-g(2.1)-PEG(2) in HEPES at concentration of 0.25 g/liter. A force of 2 Newtons was applied. A steel pin was used in each experiment. The different sliding surfaces were silicon wafer (squares), glass (circles), and steel (triangles).

25           Figure 8 is a pictorial representation of the ball-on-disk geometry used in testing the lubricant formulations in rolling geometry.

          Figure 9 is a graph of mean rolling speed (mm/sec) versus friction coefficient ( $\mu$ ) for pure buffer (HEPES), PLL(20)-g[3.4]-PEG(2) and  
30           PLL(20)-g[3.4]-PEG(5) for a steel ball rolling on a glass disk at a slide-roll ratio of 10.

## DETAILED DESCRIPTION OF THE INVENTION

### I. Copolymers

The copolymers, are graft copolymers which contain a polyionic backbone, either polycationic or polyanionic, with non-interactive side chains, such as poly(ethylene glycol)-based side chains (see Figure 1A). The copolymers are block copolymers. The copolymers may be in the form of: (1) brush copolymers (as in a bottle brush, with a backbone of one composition and bristles of another) with a backbone of poly(B) and bristles composed of poly(A),  $(A)_x-b-(B)_y$ ; (2) AB block copolymers, i.e.,  $(A)_x(B)_y$ , or a poly(A) connected at one end to a poly (B); and (3) ABA block copolymers, i.e.,  $(A)_x(B)_y(A)_z$ , or a poly(B) connected at both ends to poly(A) chains, or  $(B)_x(A)_y(B)_z$ ; where A is a monomer, the polymer of which does not bind strongly to a tissue; B is a monomer, the polymer of which does bind strongly to a tissue; x is an integer of greater than or equal to 5; y is an integer of greater than or equal to 3; and z is an integer greater than or equal to zero. Poly(A) and poly(B) are generally linear polymers, although both may be linear or branched. Both A and B can be monomers, macromers or polymers.

Suitable copolymers are described in U.S. Patent Nos. 5,462,990 and 5,627,233 and WO 98/47948 all to Hubbell *et al.* U.S. Patent Nos. 5,462,990 and 5,627,233 disclose multifunctional polymers, which include a tissue-binding component (polyionic) and a tissue non-binding component. In particular, Hubbell discloses PEG/PLL copolymers with molecular weights greater than 300 and structures that include AB copolymers, ABA copolymers, and brush-type copolymers. WO 98/47948 describes graft copolymers that attach to biological and non-biological samples to control cell-surface, cell-cell and tissue-surface interactions in biomedical applications. WO 00/065352 by Hubbell *et al.* describes polyionic coatings in analytical and sensor devices.

#### i. Polyionic Backbone

The backbone may be poly(cationic) or poly(anionic). Suitable poly(cationic) polymers have a net positive charge at neutral pH and include

polyamines having amine groups on either the polymer backbone or the polymer sidechains, such as poly-L-lysine and other positively charged polyamino acids of natural or synthetic amino acids or mixtures of amino acids, including poly(D-lysine), poly(ornithine), poly(arginine), and poly(histidine), and nonpeptide polyamines such as poly(aminostyrene), poly(aminoacrylate), poly (N-methyl aminoacrylate), poly (N-ethylaminoacrylate), poly(N,N-dimethyl aminoacrylate), poly(N,N-diethylaminoacrylate), poly(aminomethacrylate), poly(N-methyl aminomethacrylate), poly(N-ethyl aminomethacrylate), poly(N,N-dimethyl aminomethacrylate), poly(N,N-diethyl aminomethacrylate), poly(ethyleneimine), polymers of quaternary amines, such as poly(N,N,N-trimethylaminoacrylate chloride), poly(methyacrylamidopropyltrimethyl ammonium chloride), and natural or synthetic polysaccharides such as chitosan.

Suitable polyanionic blocks include natural and synthetic polyamino acids having net negative charge at neutral pH. A representative polyanionic block is poly(glutamic acid), which contains carboxylic acid side chains with a negative charge at pH 7. Glycolic acid is just one example. It may be replaced by other natural or unnatural monomers that can be polymerized and contain a side functional group with negative charge at or near neutral pH, for example, any polymer having carboxylic acid groups attached as pendant groups. Suitable materials include alginate, carrageenan, furcellaran, pectin, xanthan, hyaluronic acid, heparin, heparan sulfate, chondroitin sulfate, dermatan sulfate, dextran sulfate, poly(meth)acrylic acid, oxidized cellulose, carboxymethyl cellulose and crosmarmelose, synthetic polymers and copolymers containing pendant carboxyl groups, such as those containing maleic acid or fumaric acid in the backbone. Polyaminoacids of predominantly negative charge are particularly suitable. Examples of these materials include polyaspartic acid, polyglutamic acid, and copolymers thereof with other natural and unnatural amino acids. Polyphenolic materials such as tannins and lignins can also be used. Preferred materials include alginate, pectin, carboxymethyl cellulose, heparin and hyaluronic acid.



The choice of positively charged (cationic) (see Figures 1A and 1B) or negatively charged (anionic) (see Figures 1C and 1D) backbone is based on the type of surface to which the copolymer is to be applied. Surfaces often possess a positive or negative charge when exposed to an aqueous environment. In particular, metal oxides (such as those present on a steel or titanium surface) or metal oxide coatings exposed to an aqueous solution spontaneously acquire a negative charge at pH above the isoelectric point (IEP) and positive charges at pH below the isoelectric point of the particular oxide chosen. For example, at pH 7 (neutral solution), niobium oxide (Nb<sub>2</sub>O<sub>5</sub>), tantalum oxide or titanium oxide (TiO<sub>2</sub>) are all known to be negatively charged, while aluminum oxide at pH 7 is positively charged. The opposite charges of polymer and surface lead to a strong electrostatic binding of the polymer backbone to the surface, allowing the PEG chains to protrude into the solution, forming a lubricious coating.

#### 15                   ii. Non-Interactive Polymers

"Non-interactive" indicates that the polymer does not interact or bind with the metal oxide surfaces. Suitable non-interactive polymers include polyalkylene oxides, such as poly(ethylene glycol) (PEG), mixed polyalkylene oxides having a solubility of at least one gram/liter in aqueous solutions such as some poloxamer nonionic surfactants, neutral water-soluble polysaccharides, polyvinyl alcohol, poly-N-vinyl pyrrolidone, non-cationic poly(meth)acrylates, many neutral polysaccharides, including dextran, ficoll, and derivatized celluloses, such as hydroxy ethyl cellulose, polyvinyl alcohol, non-cationic polyacrylates, such as poly(meth)acrylic acid, and esters amide and hydroxyalkyl amides thereof, and neutral poly(amino acids) such as poly(serine), poly(threonine), and poly(glutamine) and copolymers of the monomers thereof, and combinations thereof.

In the preferred embodiment, the non-interactive polymer is poly(ethylene glycol) (PEG). PEG chains are highly water-soluble and highly flexible. PEG chains have an extremely high motility in water and are essentially non-ionic in structure. The PEG chains are grafted onto the polyionic backbone to form a copolymer.

### iii. Modified Copolymers

The copolymer can be modified by introducing functional groups at or near the terminal (free end) position of the side chains. These groups allow further functionalization and incorporation of species that have an additional beneficial effect on the tribological behavior. In one embodiment, bioactive molecules, such as biotin, are added to the terminal end of the PEG chains (see e.g. Figures 1B and 1D). Other linker species, such as thiol, NTA (for binding to histidine-tags via Ni ions), and vinylsulfone can also be used.

A modified copolymer has three functions: (1) charged sites in the backbone used to attach the molecule to oppositely charged substrate surfaces (called 'substrate attachment function'), (2) grafted side chains that form a dense structure, such as a brush, to make the surface lubricious, and (3) functional groups that allow the incorporation of further molecules, which have advantageous tribological properties.

Non-modified and modified copolymers can be used singly, consecutively or as a mixture.

### iv. Aqueous solutions

The aqueous solution may be a lubricant, such as water or buffer solutions such as HEPES. Other additives, such as compounds which inhibit rust and corrosion, may also be present.

### II. Methods of Making the Lubricant Compositions

The copolymers are dissolved in an aqueous medium at a low concentration. The polymers are added to form a solution with a concentration of 0.1 g/liter to 10g/liter. In a preferred embodiment, the concentration range is 0.25 g/liter to 2 g/liter.

Additives to prevent corrosion and rust may be present in the solution.

### III. Methods of Using the Lubricant Compositions

The lubricant compositions may be applied to charged surfaces to form a lubricious coating on the surfaces. This results in a lower friction coefficient between two sliding surfaces under boundary lubrication

conditions, as well as the protection of the surfaces from wear. As shown in Figure 2, the charged backbone of the copolymers adsorbs onto the surface, while the PEG sidechains generally extend away from the surface. The PEG sidechains may be modified to contain functional molecules (depicted as dots in Figure 2) at the end of the chain which allow for the specific interaction with other molecules.

Any system where a metal oxide film is present, such as steel, aluminum, titanium, glass, silicon, may be coated with the lubricant compositions. Such systems favor aqueous solutions over oil-based ones. Devices or machines used in the textile or food and beverage industry, for example, where contamination from oil is a problem, may be coated with the lubricant compositions.

The present invention will be further understood by reference to the following non-limiting examples.

#### Examples

##### **Example 1: Adsorption of PLL(375)-g[5.6]-PEG(5) on metal oxide surfaces.**

PLL(375)-g[5.6]-PEG(5) or PLL(20)-g[3.4]-PEG(2) was added to 10 mM organic buffer, 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) at pH 7.4, to form a 1 mg/mL polymer solution. Measurements were taken by the optical waveguide lightmode spectroscopy (OWLS) method.

Figure 3 displays the uptake of PLL(20)-g[3.4]-PEG(2) solutions on a steel surface (magnetron sputtered onto a waveguide surface) as a function of time, thereby showing that the polymer attaches itself to the surface, forming a surface coverage of some 200 ng/cm<sup>2</sup> after a short period. Figure 4 displays the total uptake of PLL(375)-g[5.6]-PEG(5) on several oxides surfaces, showing the dependence of the amount of uptake on the isoelectric point of the oxide surface.

**Example 2: Lubrication of Steel Pin against Glass with PLL-g-PEG Copolymers (Sliding Geometry).**

Two different architectures of PLL-PEG (PLL(20)-g[3.4]-PEG(2) and PLL(20)-g[3.4]-PEG(5)) were dissolved in HEPES at a concentration of 0.25 g/liter and used to lubricate a couple consisting of a steel pin and glass. The steel is covered with its native oxide.

The contact geometry for testing lubricant formulations is shown in Figure 5. The lubricant was placed on the surface of the glass and the steel pin was then placed on top of the glass and the glass disk rotated to create a sliding motion between the two surfaces. The glass and the pin were also tested in a polymer-free buffer.

In Figure 6, the sliding-friction-reduction effect of the added polymer is seen when the polymer-containing solution is compared to the polymer-free buffer. The friction coefficient ( $\mu$ ) of buffer (0.28) is reduced to a value of 0.13 for PLL(20)-g[3.4]-PEG(2) and to a value of 0.11 for PLL(20)-g[3.4]-PEG(5). Thus, a friction-reducing effect is observed. These results also indicate that the reduction in friction increases as the length of the side chains (e.g. PEG) increases.

**Example 3: Lubrication of three different sliding pairs, Steel-Glass, Steel-Silicon, and Steel-Steel, with PLL-PEG graft copolymer.**

The PLL(20)-g(2.1)-PEG(2), polymer was added to HEPES at 0.25 g/liter. A steel pin was used in each experiment, and a force of 2 Newtons was applied. The contact geometry for testing the lubricant formulation is shown in Figure 5. The friction-reducing effect observed on three different sliding pairs, steel-glass, steel-silicon, and steel-steel (Figure 7). The friction-reduction effects are noticeable on all three couples. For the steel-silicon couple, the friction coefficient decreased from 0.21 without the polymer to 0.12 with the polymer solution. For the steel-glass couple, the friction coefficient reduced even more drastically, from 0.36 without the polymer to 0.09 with the polymer solution. For the steel-steel couple, the friction coefficient was reduced from 0.36 without the polymer to 0.22 with the polymer solution.

**Example 4: Lubrication of Steel Ball against Glass with PLL-g-PEG Copolymers (Rolling Geometry).**

Two different architectures of PLL-PEG (PLL(20)- g[3.4]-PEG(2) and PLL(20)-g[3.4]-PEG(5)) were dissolved in HEPES at a concentration of 0.25 g/liter and used to lubricate a couple consisting of a steel pin and soda glass. The steel was covered with its native oxide.

The contact geometry for testing lubricant formulations is shown in Figure 8. The lubricant was placed on the surface (10) of the glass disk and the steel ball (15) was then placed on top of the glass. The glass disk (20) and the steel ball (15) were both rotated, creating a mixed rolling/sliding contact, with a slide/roll ratio of 10 (chiefly rolling). The glass (20) and the ball (10) were also tested in a polymer-free buffer (HEPES).

The results of this test are shown in Figure 9. The friction-reduction effect of the added polymer is compared to the performance of pure buffer. A friction-coefficient -reduction effect of greater than two orders of magnitude was observed when polymer was added to the buffer. Further, the longer PEG chains (PLL(20)- g[3.4]-PEG(5)) provided nearly an extra order of magnitude effect over the short-chain version of the polymer (PLL(20)-g[3.4]-PEG(2)).

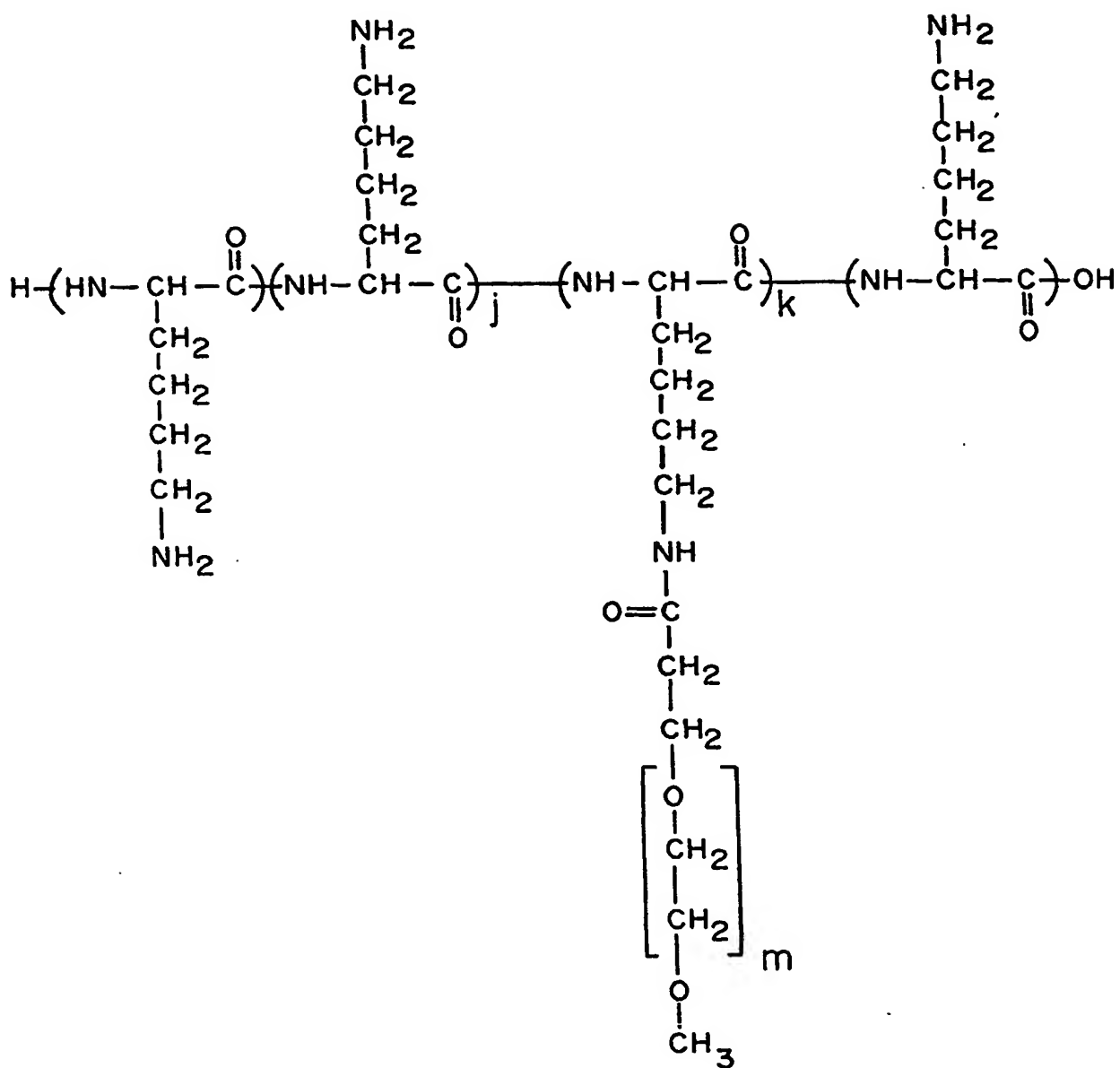
It is understood that the disclosed invention is not limited to the particular methodology, protocols, and reagents described as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims.

We claim:

1. A method of lubricating a charged surface, comprising administering a lubricating composition to the surface, wherein the lubricating composition comprises a graft copolymer with a polyionic backbone and non-interactive side chains and an aqueous medium.
2. The method of claim 1, wherein the polyionic backbone is poly(cationic).
3. The method of claim 2, wherein the polyionic backbone is selected from the group consisting of polyamino acids and polysaccharides having net positive charge at neutral pH.
4. The method of claim 3, wherein the polyionic backbone is poly-L-lysine.
5. The method of claim 1, wherein the polyionic backbone is poly(anionic).
6. The method of claim 5, wherein the polyionic backbone is a polyamino acid having net negative charge at neutral pH.
7. The method of claim 6, wherein the polyamino acid is poly(L-glutamic acid).
8. The method of claim 1, wherein the non-interactive side chains are poly(ethylene glycol) chains.
9. The method of claim 8, wherein the poly(ethylene glycol) chains are modified to contain a functional group at the free end.
10. The method of claim 9, wherein the copolymer further comprises biotin, wherein the biotin is attached to at least one poly(ethylene glycol) chain.
11. The method of claim 1, wherein the charged surface is a metal oxide.
12. A lubricated surface, comprising a charged surface and lubricating composition, wherein the lubricating composition comprises a graft copolymer with a polyionic backbone and non-interactive side chains and an aqueous medium.
13. The lubricated surface of claim 12, wherein the lubricating composition is PLL-g-PEG.

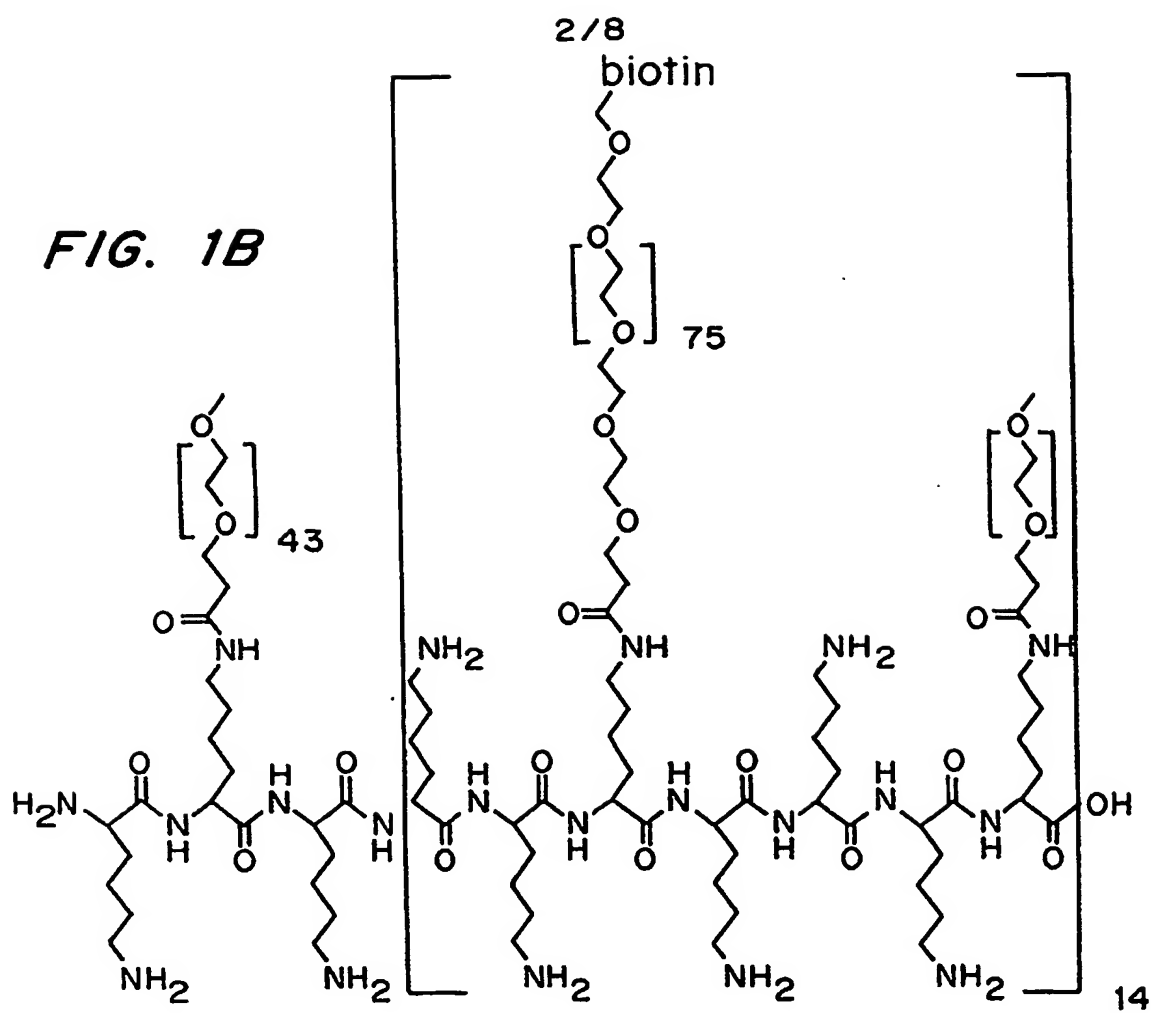
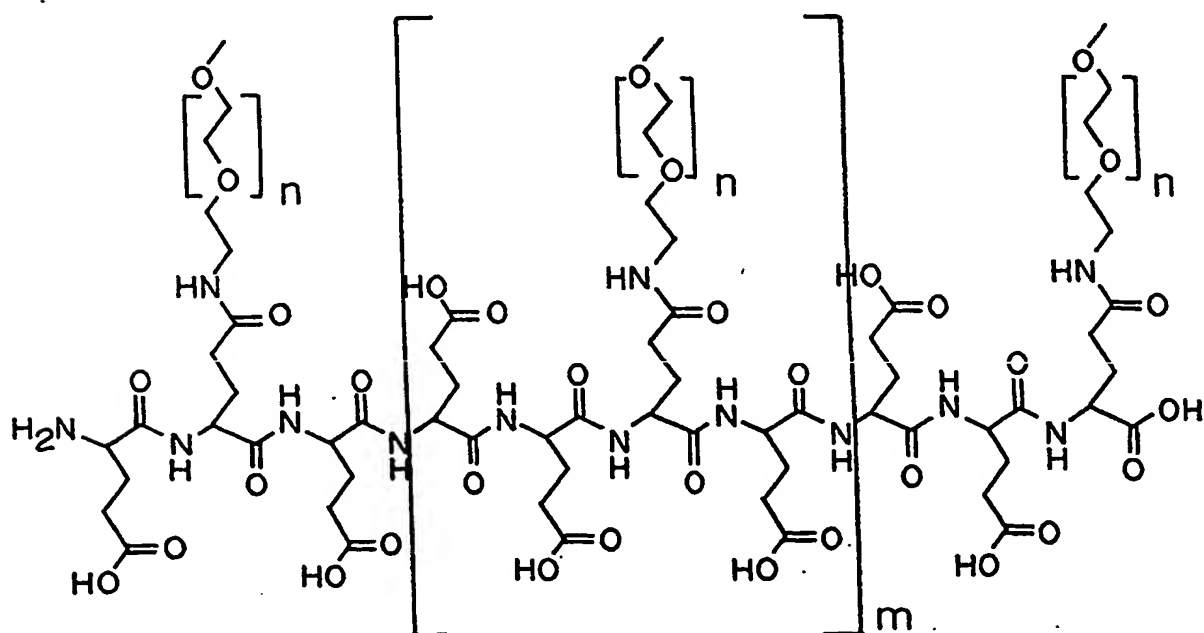
14. The lubricated surface, wherein the charged surface is a metal oxide.
15. A method of lubricating a charged surface comprising on its surface a graft copolymer with a polyionic backbone and non-interactive side chains and an aqueous medium, comprising providing an aqueous solution to the device.

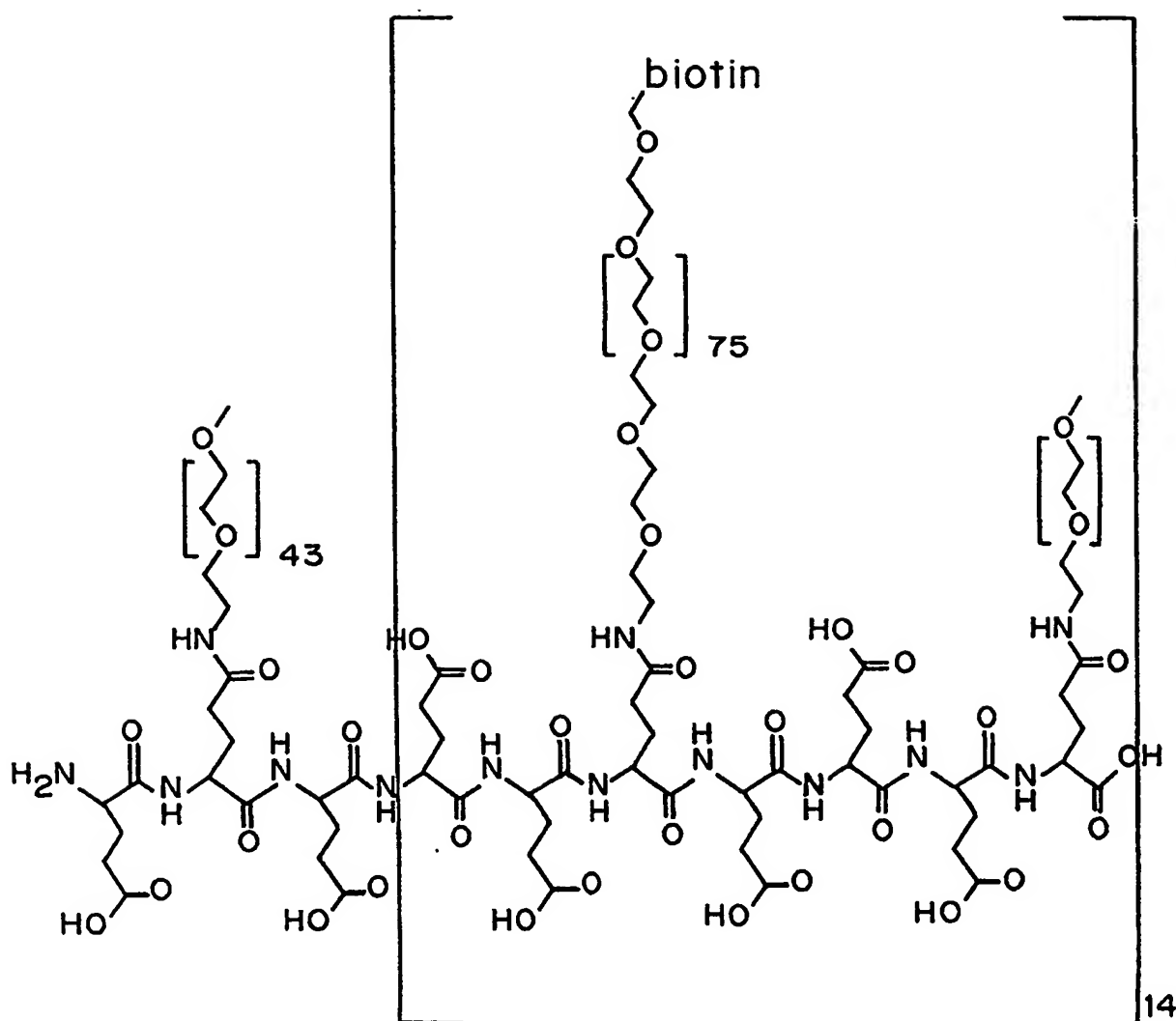
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**FIG. 1A**

SUBSTITUTE SHEET (RULE 26)



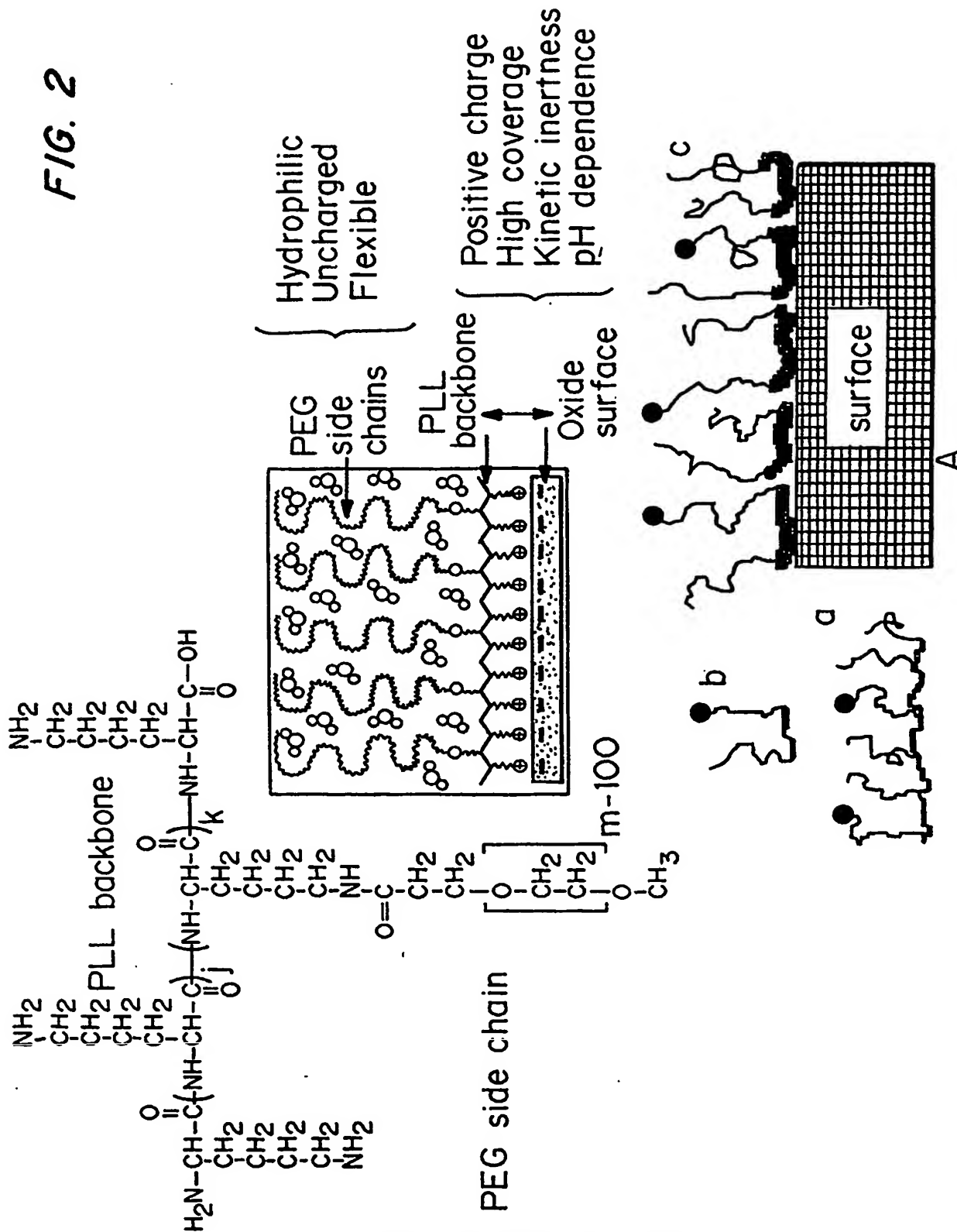
**FIG. 1B****FIG. 1C**



**FIG. 1D**

**SUBSTITUTE SHEET (RULE 26)**

FIG. 2



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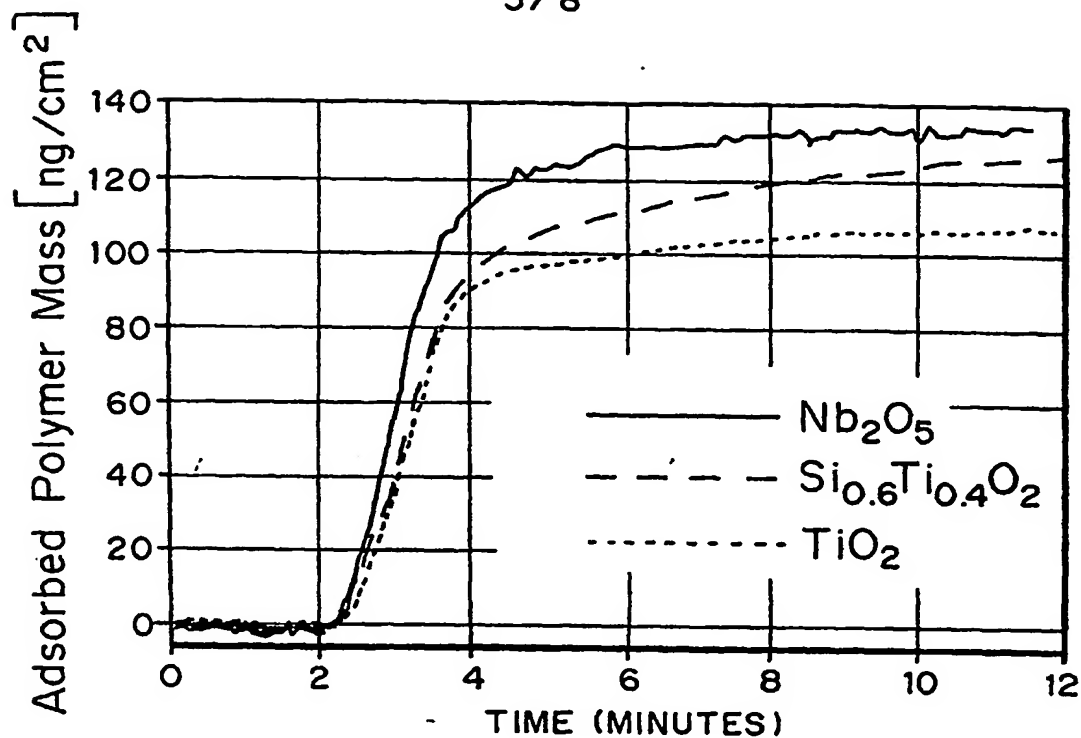


FIG. 3

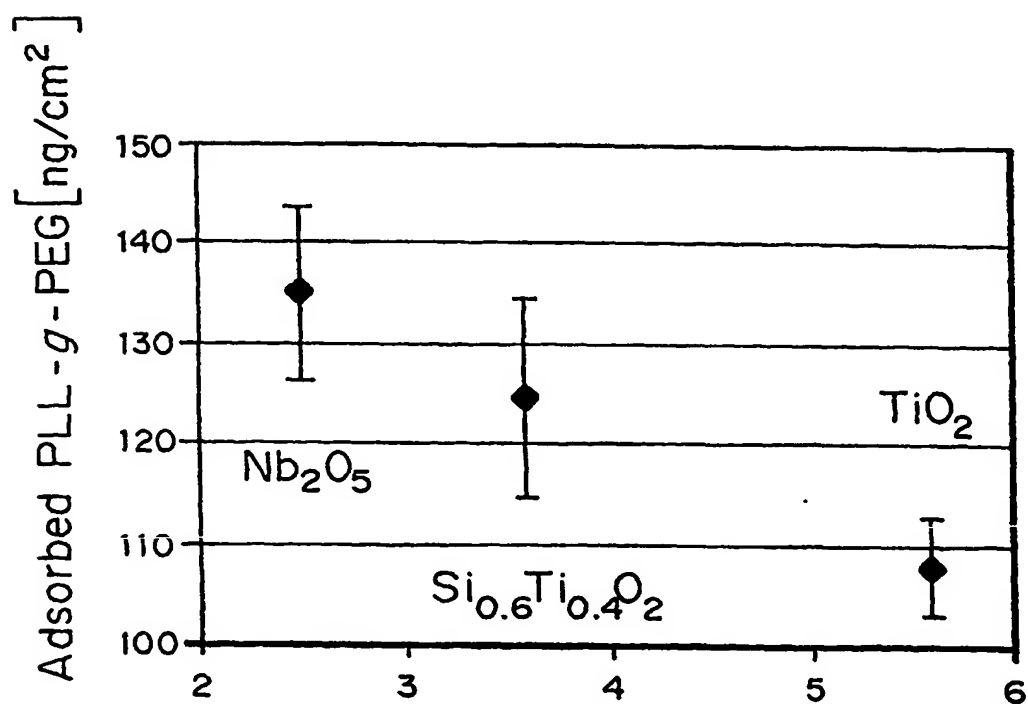
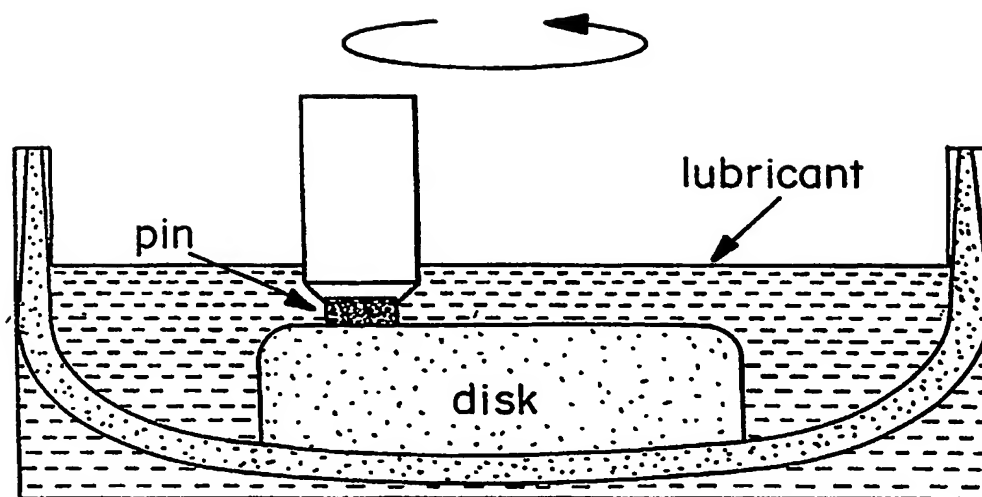
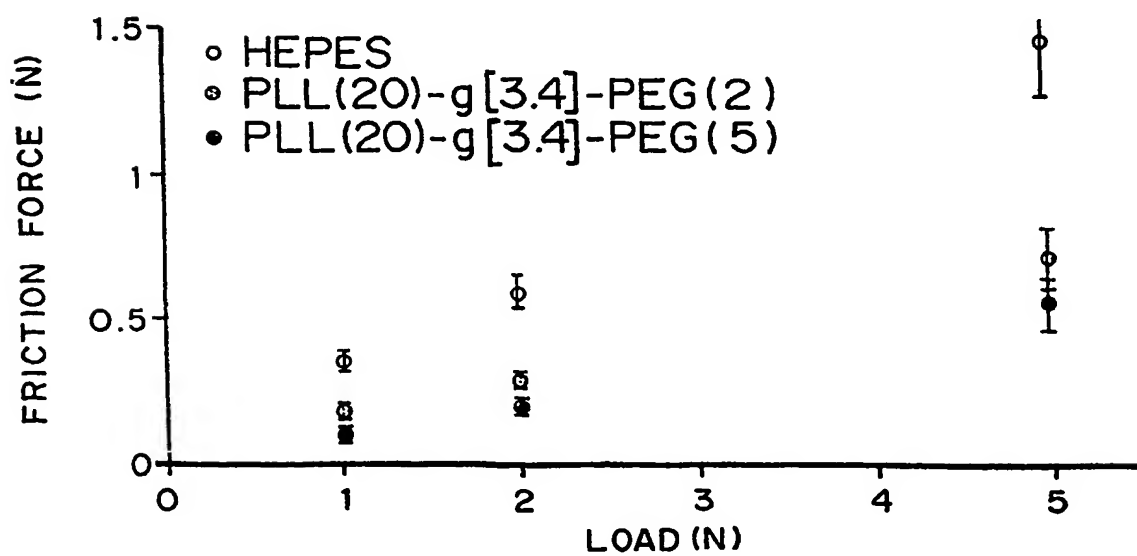


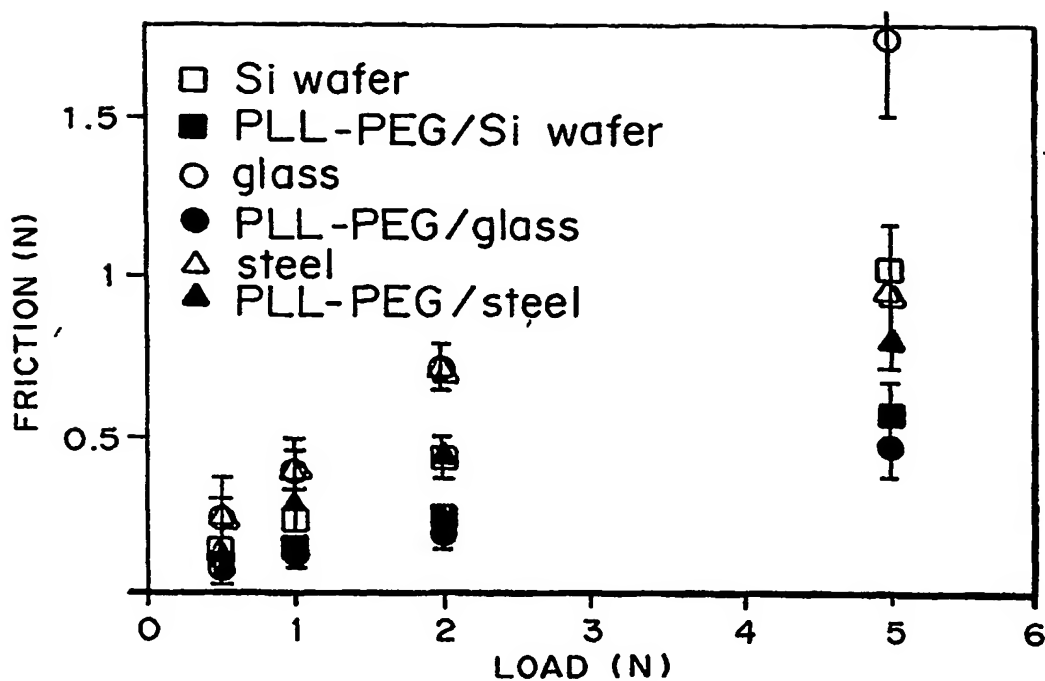
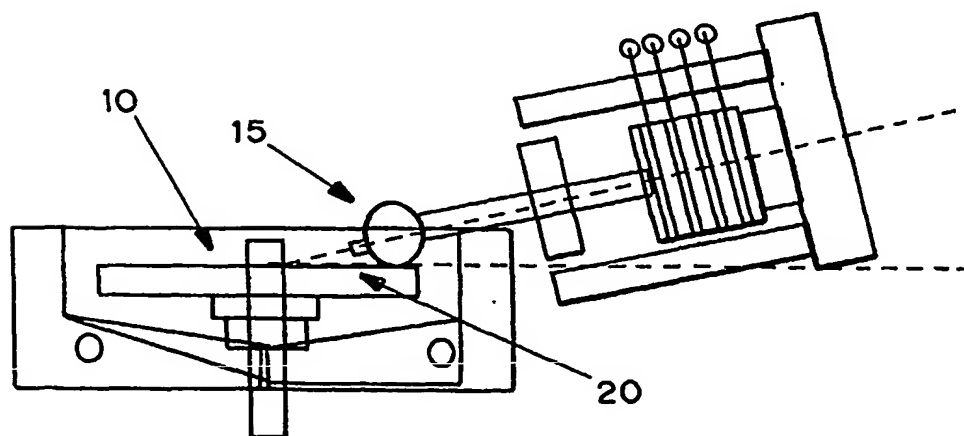
FIG. 4

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**FIG. 5****FIG. 6**

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**FIG. 7****FIG. 8**

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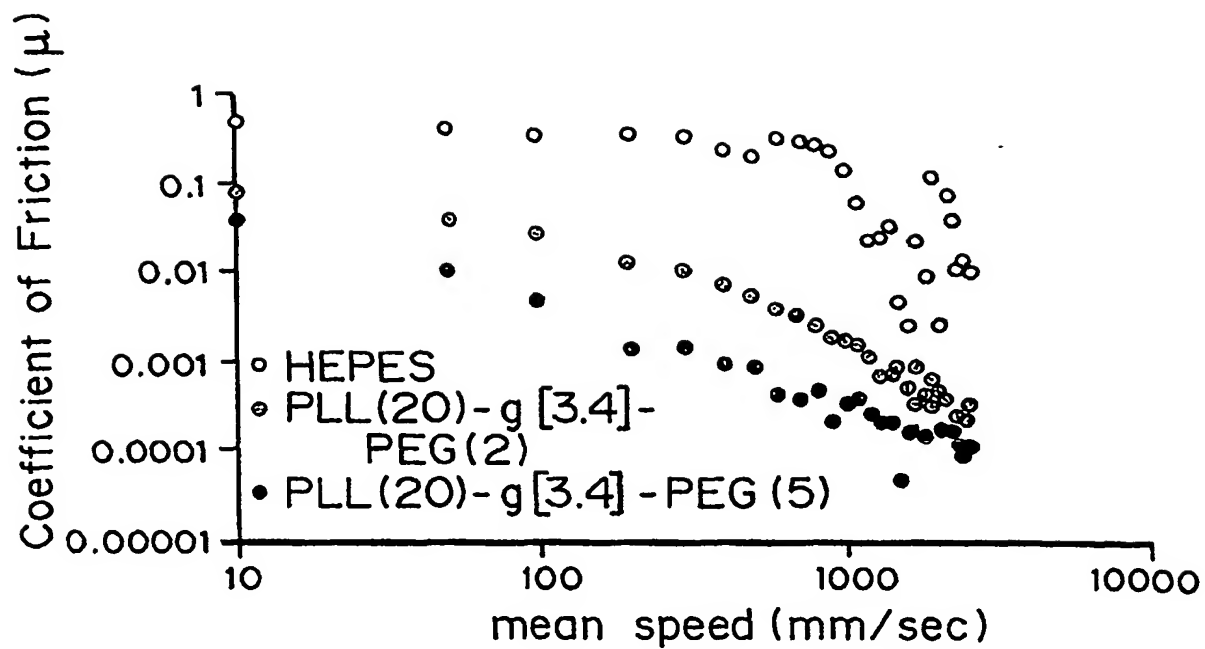


FIG. 9